

# PATENT SPECIFICATION

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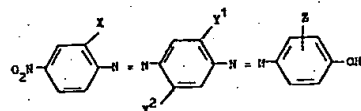


## (54) DISPERSE NITRO DISAZO DYESTUFFS

(71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, Imperial Chemical House, Millbank, London SW1P 3JF, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to disperse disazo dyestuffs which are valuable for colouring synthetic textile materials, particularly aromatic polyester textile materials.

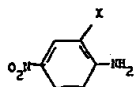
According to the invention there are provided the disperse disazo dyestuffs of the formula:—



wherein X is hydrogen, methyl, chlorine or bromine, one of Y<sup>1</sup> and Y<sup>2</sup> is methyl and the other of Y<sup>1</sup> and Y<sup>2</sup> is hydrogen or methyl, and Z is hydrogen or methyl.

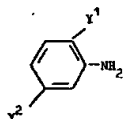
Preferably X is hydrogen.

According to a further feature of the invention there is provided a process for the manufacture of the disazo dyestuffs of the invention which comprises diazotising an amine of the formula:—



Formula I

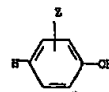
coupling with an amine of the formula:—



Formula II

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or the  $\omega$ -methane sulphonate derivatives thereof with subsequent hydrolysis, rediazotising and coupling on to a coupling component of the formula:—



Formula III

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wherein X, Y<sup>1</sup>, Y<sup>2</sup> and Z have the meanings stated.

The process of the invention can be conveniently carried out by, for example, adding sodium nitrite to a solution or suspension of the amine of Formula I in an aqueous solution of a strong inorganic acid such as hydrochloric acid, adding the resulting solution or suspension of the diazo compound to a solution of the amine of Formula II, or the corresponding  $\omega$ -methane sulphonate, in an aqueous solution of an acid. If necessary the pH of the resulting mixture is adjusted to facilitate coupling, and the mixture is then stirred, preferably at a temperature between 0° and 15°C, until coupling is complete. The resulting monoazo compound is then filtered off, and when starting from the  $\omega$ -methane sulphonate this group is removed by treatment in a hot aqueous solution of an alkali. The resulting aminoazo compound is stirred in an aqueous solution of a strong inorganic acid optionally containing acetic acid, sodium nitrite is added, and when diazotisation is complete the solution or suspension of the diazo compound is added to an aqueous alkaline solution of the coupling component. Coupling is then effected at a pH above 7, and the resulting disazo dyestuff is isolated in conventional manner.

If desired the second diazotisation and subsequent coupling can be carried out without intermediate isolation of the aminoazo compound.

The amines of Formula I are 4-nitro-2-methylaniline, 4-nitro-2-chloroaniline, 4-nitro-2-bromoaniline, and above all 4-nitroaniline.

As examples of the amines of Formula II or the corresponding  $\omega$ -methane sulphonates there may be mentioned 2:5-dimethylaniline (*p*-xylydine), *o*-toluidine and *m*-toluidine  $\omega$ -methane sulphonate.

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The coupling components of Formula III are phenol, *o*-cresol or *m*-cresol.

The disazo dyestuffs of the invention are valuable for colouring synthetic textile materials such as cellulose acetate textile materials, but more especially aromatic polyester textile materials. The said dyestuffs can be applied to synthetic textile materials by the methods which are conventionally employed in applying disperse dyestuffs to such textile materials. When so applied the dyestuffs yield orange shades. The dyestuffs have good affinity and build-up properties on aromatic polyester textile materials thus enabling heavy depths of shade to be obtained, and the resulting colourations have good fastness to light, to wet treatments, perspiration, to rubbing, and to dry heat treatments.

The invention is illustrated but not limited by the following Examples in which the parts and percentages are by weight.

#### Example 1.

A solution of 13.8 parts of *p*-nitroaniline in a mixture of 36 parts of water and 120 parts of a concentrated aqueous solution of hydrochloric acid is cooled to 5°C, and 60 parts of a 14% aqueous solution of sodium nitrite added at 5° to 10°C. The mixture is stirred for 15 minutes at the same temperatures and excess nitrous acid destroyed by the addition of sulphamic acid. The resulting solution of the diazo compound is then added to a solution of 24.53 parts of *m*-toluidine  $\omega$ -methane sulphonate in a mixture of ice and water containing 12 parts of a concentrated aqueous solution of hydrochloric acid, and the pH of the mixture is then raised to 4 by the addition of sodium acetate. The mixture is stirred for 15 minutes and the precipitated solid is filtered off and washed with water. The resulted solid is then stirred for 2 hours in 3200 parts of a 2% aqueous solution of sodium hydroxide at 60°C, and the precipitated aminoazo compound is filtered off, washed with water and dried.

25.6 parts of the aminoazo compound are stirred in a mixture of 200 parts of acetic acid and 24 parts of a concentrated aqueous solution of hydrochloric acid at 10°C, and 60 parts of a 14% aqueous solution of sodium nitrite are added. The mixture is stirred for 60 minutes at 5°—10°C, and excess nitrous acid destroyed by addition of sulphamic acid. The resulting solution of the diazo compound is then added to a solution of 11.88 parts of *o*-cresol in 60 parts of an 8% aqueous solution of sodium hydroxide, the temperature being maintained below 5°C by the addition of ice, and the pH at 7—8 by the simultaneous addition of a 10% aqueous

solution of sodium carbonate. The mixture is stirred for 15 minutes and the precipitated dyestuff is filtered off, washed with water and dried.

When dispersed in aqueous medium the dyestuff dyes aromatic polyester textile materials in orange shades of good fastness properties.

#### Example 2.

13.8 parts of *p*-nitroaniline are diazotised as described in Example 1, and the resulting solution of the diazo compound is added to a solution of 16.06 parts of 2:5-dimethylaniline hydrochloride in water containing ice. The pH of the mixture is adjusted to 4 by the addition of sodium acetate, and, after stirring for 15 minutes, the precipitated aminoazo compound is filtered off, washed with water and dried.

27.0 parts of the aminoazo compound are stirred in a mixture of 200 parts of acetic acid and 24 parts of a concentrated aqueous solution of hydrochloric acid at 10°C, and 60 parts of a 14% aqueous solution of sodium nitrite are added. The mixture is stirred for 60 minutes at 5°—10°C, and excess nitrous acid destroyed by addition of sulphamic acid. The resulting solution of the diazo compound is then added to a solution of 11.88 parts of *o*-cresol in 60 parts of an 8% aqueous solution of sodium hydroxide, the temperature being maintained below 5°C by the addition of ice, and the pH at 7—8 by the simultaneous addition of a 10% aqueous solution of sodium carbonate. The mixture is stirred for 15 minutes and the precipitated dyestuff is filtered off, washed with water and dried.

When dispersed in aqueous medium the dyestuff dyes aromatic polyester textile materials in orange shades of good fastness properties.

#### Example 3.

In place of the *p*-xylydine hydrochloride and/or *o*-cresol used in Example 2 there are used respectively equivalent amounts of *o*-toluidine hydrochloride and/or phenol, when similar dyestuffs are obtained.

The following Table gives further Examples of the dyestuffs of the invention which are obtained by diazotising the amines listed in the second column of the Table, coupling on to the amines (i.e. middle components) listed in the third column of the Table, rediazotising and coupling on to the coupling components listed in the fourth column of the Table using methods similar to that described in Examples 1 and 2. The fifth column of the Table lists the shades obtained from the resulting dyestuffs.

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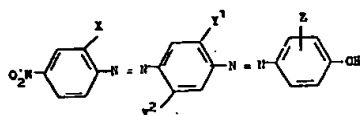
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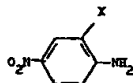
Example	Amine	Amine (middle components)	Coupling Component	Shade
4	2-chloro-4-nitroaniline	<i>p</i> -xylydine	<i>o</i> -cresol	Reddish-orange
5	2-bromo-4-nitroaniline	"	"	"
6	2-methyl-4-nitroaniline	"	"	Orange
7	4-nitroaniline	"	<i>m</i> -cresol	"
8	"	"	phenol	Orange-brown
9	"	<i>m</i> -toluidine	"	"
10	"	"	<i>m</i> -cresol	Orange
11	"	<i>o</i> -toluidine	"	"
12	2-chloro-4-nitroaniline	<i>p</i> -xylydine	phenol	"
13	2-methyl-4-nitroaniline	"	"	"
14	2-bromo-4-nitroaniline	"	<i>o</i> -cresol	"

## WHAT WE CLAIM IS:—

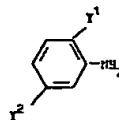
1. The disperse disazo dyestuffs of the formula:—



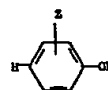
- 5 wherein X is hydrogen, methyl, chlorine or bromine, one of Y<sup>1</sup> and Y<sup>2</sup> is methyl and the other of Y<sup>1</sup> and Y<sup>2</sup> is hydrogen or methyl, and Z is hydrogen or methyl.
- 10 2. The disperse disazo dyestuffs as claimed in Claim 1 wherein X is hydrogen.
3. The disperse disazo dyestuffs as claimed in Claim 1 or Claim 2 substantially as described herein and shown with reference to any one of the Examples.
- 15 4. Process for the manufacture of the disperse disazo dyestuffs as claimed in Claim 1 which comprises diazotising an amine of the formula:



- 20 coupling with an amine of the formula:



or the  $\omega$ -methane sulphonate derivative thereof with subsequent hydrolysis, re-diazotising and coupling on to a coupling component of the formula:



wherein X, Y<sup>1</sup>, Y<sup>2</sup> and Z have the meanings stated in Claim 1.

5. Process for the manufacture of the disperse disazo dyestuffs as claimed in any one of Claims 1 to 3 substantially as described herein and shown with reference to any one of the Examples.

6. Process for colouring synthetic textile materials which comprises applying thereto a disperse disazo dyestuff as claimed in any one of Claims 1 to 3.

D. VINCENT.  
Agent for the Applicants.